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# Effects of heavy metal wastewater on the anoxic/aerobic-membrane bioreactor bioprocess and membrane fouling

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## HIGHLIGHTS

- Heavy metals had less impact on denitrification than on nitrification.
- SEM images, EDX, and AAS analysis showed heavy metals in the cake layer.
- Heavy metals had a negative effect on membrane fouling.

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## ABSTRACT

Heavy metals have significant negative effects on anoxic/aerobic-membrane bioreactors (A/O-MBR). The changes in the performance of A/O-MBR fed with municipal wastewater containing 0.25–2.56 mg/L (low concentrations) and 3.7–32.3 mg/L (high concentrations) of zinc, copper, lead, and cadmium were studied in this paper. The nitrification rate decreased to 27% and 46%, whereas the denitrification rate decreased to 20% and 34% under treatment with low/high concentrations of heavy metals, which indicate that heavy metals more significantly affect nitrification than denitrification. Heavy metals also resulted in the increase of carbohydrate of extracellular polymer substances and a smaller particle size distribution. Scanning electron microscope images, energy-dispersive X-ray spectroscopy and atomic absorption spectrometry analysis of fouled membranes showed solid inorganic scale deposits on the membrane. All these results suggest that heavy metals affect membrane fouling in two ways: (a) modification of sludge characteristics; and (b) contribution to inorganic fouling.



## 1. Introduction

Toxic metals are almost ubiquitous in wastewater, because of their diverse range of sources (Santos and Judd, 2010). Although industrial activities have always been significant source of heavy metals, more dilute and diffuse sources such as traffic-related emissions, effluents from small businesses, domestic effluents, and several other chemical treatment processes have become important sources of heavy metal emission (Karvelas et al., 2003). The effects of metals on conventional activated sludge processes have been extensively studied over the past 30 years from biodegradation inhibition to biological nutrient removal inhibition, and biosorption (Santos and Judd, 2010). Membrane bioreactor (MBR) technology is widely recognized as offering a key option for the enhancement of wastewater treatment or reuse as well as enables the efficient removal of biological oxygen demand (BOD) and chemical oxygen demand (COD), water reclamation and low footprint (Fangang et al., 2009; Mutamim et al., 2012). The widespread application of MBR, makes the effect of heavy metals on MBRs is an inevitable and valuable issue to discuss. Previous works focused on the heavy metals removal achieved by MBRs. Malamis et al. (2010) discovered that Ultrafiltration (UF) membranes combined with sludge facilitated the significant removal of Cu(II) and Ni(II) from industrial wastewater, achieving removal efficiencies of 59–78% and 23–50% respectively. Bolzonella et al. (2010) noted that an MBR system can improve the removal efficiency for heavy metals 10–15% compared with the conventional activated sludge system. The influent heavy metal concentrations in these works were very low (<1 mg/L). To evaluate the effect of high concentrations of heavy metal on MBR, Katsou et al. (2011) examined an addition of 3–15 mg/L of Cu(II), Pb(II), Ni(II), and Zn(II) in an MBRs and found that the addition of these heavy metals resulted in a lower, but satisfactory COD removal and significantly affected nitrification. Malamis et al. (2012) observed a significant decrease of the heterotrophic and autotrophic biomass activity when 4–12 mg/L of heavy metals is introduced in an MBR-reverse osmosis (RO) system which achieved excellent heavy metals removal

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efficiency. In the aforementioned works, however, there is limited information is available on the effects of heavy metals on MBR performance which largely falls into two aspects: (a) the inhibition effect of heavy metals on MBR biological performance; and (b) the negative effect of heavy metals on membrane fouling. The main limitations of an MBR is membrane fouling, which can be attributed to both membrane pore clogging and sludge cake deposition on the membrane surface, in which the cake layer is usually the predominant fouling component (Mutamim et al., 2012). Activated sludge particle size distribution (PSD) and extracellular polymeric substances (EPS) are important sludge characteristics that significantly affect membrane fouling (Tian and Su, 2012; Wang et al., 2009). Wu et al. (2011) found that more serious cake fouling correlated with the activated sludge characteristics such as smaller floc size and greater EPS amount. Therefore, testing the effect of heavy metals on sludge EPS and PSD is reasonable.

The effect of heavy metals on membrane fouling is a complex issue that has seldom been investigated. Many previous works have found that metals cause inorganic fouling. Wang et al. (2008) observed that organic substances and inorganic elements such as Mg, Al, Fe, Ca, and Si form the cake layer. Lyko et al. (2007) also found that metal substances more significantly contribute to membrane fouling compared with biopolymers. The effect of heavy metals on membrane fouling may be different from that of conventional metals because the former not only directly affects the membrane but also significantly affects sludge characteristics. Heavy metals may sometimes enter domestic and/or industrial wastewater. The evaluation of effect of these heavy metals on MBR is therefore of great practical significance. Moreover, the effects of low/high concentrations of heavy metals on sludge characteristics and membrane fouling are significant but have seldom been studied in the aforementioned works. Copper, lead, zinc, and cadmium, which are produced by a broad range of manufacturers, are among the most common polluting metal ions in industrial wastewater and are also associated with toxicity issues.

In this study, we mainly focuses on the membrane fouling caused by copper, lead, zinc, and cadmium by investigating the effects of these metals on EPS and soluble EPS as well as on sludge PSD. Moreover, the fouled membrane was analyzed using energy-dispersive X-ray (EDX) spectroscopy and an atomic absorption spectrometer was employed to measure the heavy metals in the cake layer. These were never explored in past studies. Aside from membrane fouling characteristics, the biological performance of A/O-MBR such as COD, nitrogen removal, and sludge activity was also investigated. The findings will aid in understanding the mechanism by which heavy metals affect the performance of A/O-MBR.

## 2. Methods

As shown in Supplementary Fig. S1, a pilot-scale A/O-MBR (200 L) treating daily approximately 350 L of influent wastewater daily was used in this study. A polyvinylidene fluoride (PVDF) hollow-fiber microfiltration (MF) membrane module (Tianjin Motian Membrane Engineering and Technology Co., Ltd., China) was used in the A/O-MBR. The MF membrane module is employed with a nominal pore size of 0.2 μm and an effective filtration area of 1 $m^2$ is employed. Three experimental runs were conducted in series. Primary treated municipal wastewater with Zn(II), Cu(II), Pb(II), and Cd(II) was used for this study. In the 1st run, the system was operated for a period of 33 d without the addition of any metals and under steady conditions (control conditions). In the 2nd run (days 34–93) influent containing 0.25–2.56 mg/L of heavy metals was fed into the system. In the 3rd run (days 94–131), the system was fed with influent containing 3.7–32.3 mg/L of heavy metals. The wastewater in the equalization tank was kept under continuous agitation. Coarse bubble equipment was used to reduce membrane fouling through hydrodynamic scouring in the MBR tank. The effluent was controlled using a peristaltic pump. A dissolved oxygen (DO) meter was employed to determine the DO, and the aeration rate was adjusted through the air flow meter. Flux, temperature, pH, and trans-membrane pressure (TMP) were regularly monitored. During operation, chemical cleaning was employed when the TMP reached 50 kPa by immersing the module in an NaOCl solution (1000 mg/L $Cl_2$) for 6 h and then in 4000 mg/L of citric acid solution for 4 h. Seeding sludge was supplied by a local sewage treatment plant. The A/O-MBR operating characteristics are shown in Table 1. Table 2 summarizes the biological and filtration characteristics of the system. The filtration and backwash fluxes were kept constant at 15 and 20 L/$m^2$-h, respectively, whereas the SRT and HRT of the system were 30 d and 13.6 h, respectively. The primary treated municipal wastewater used for this study that was enriched with Zn(II), Cu(II), Pb(II), and Cd(II) in multi-metal solutions was fed into the pilot-scale MBR system. Sulfate salts of the above metals were supplied. The influent wastewater characteristics for the three experimental runs are summarized in Table 2. The pH value of the system was controlled at 7.0–7.5 by adding $Na_2CO_3$.

Laboratory analyses were conducted to determine the characteristics of the influent wastewater, activated sludge, and permeate. More specifically, the COD and $NH_4$-N were measured using the microwave digestion method and Nessler's reagent spectrophotometry, respectively, whereas the presence of Zn(II), Cu(II), Pb(II),and Cd(II) was determined using an atomic absorption spectrometer (Shimadzu AA6300C). To determine the heavy metal concentrations in the MBR system, the samples were digested at 440 °C using $H_2O_2$ and $HNO_3$ and then filtered through GF/C Whatman filters. The PSD of the mixed liquor was obtained using a laser granulometer (Mastersizer 2000, Malvern instruments, UK). At the end of the operation, a piece of membrane fiber was cut from the membrane module during each run after a physical wash. The sample was fixed with 3.0% glutaraldehyde in a 0.1 M phosphate buffer at pH 7.2. The sample, dehydrated with ethanol and golden-coated by a sputter (E-1010), was observed using scanning electron microscopy (SEM) (Japan Electronic Co., JSM-6610LV). EDX analysis was then performed in used membrane fibers using the Quanta 200 of FEI to investigate metal element depositions on the membrane surface. The EPS of sludge flocs was extracted using the heating method (Chang and Lee, 1998). The extracted EPS was analyzed for total carbohydrates and proteins. Carbohydrates in the EPS (EPSc) were determined according to the phenol–sulfuric acid method with glucose as standard (Dubois et al., 1956). Proteins in the EPS (EPSp) were determined using the Folin method with bovine serum albumin (BSA) as standard (Lowry et al., 1951). The chemicals used were analytic reagent grade. The biomass inhibition experiments were conducted using the maximum specific Oxygen Uptake Rate (sOUR) and Ammonium Uptake Rate (AUR) of the activated sludge (Katsou et al., 2011). Membrane fouling was determined by calculating TMP over time.

## 3. Results and discussion

A/O-MBR biological treatment performance was assessed in terms of organics and nitrogen removal from wastewater. Heterotrophic and autotrophic biomass activities were also evaluated. To gain deeper insight into membrane fouling, the floc PSD and EPS components were also assessed.

### 3.1. Wastewater and system operating characteristics

In the 1st run, the feed wastewater was primary treated municipal wastewater without any heavy metals, whereas in the 2nd